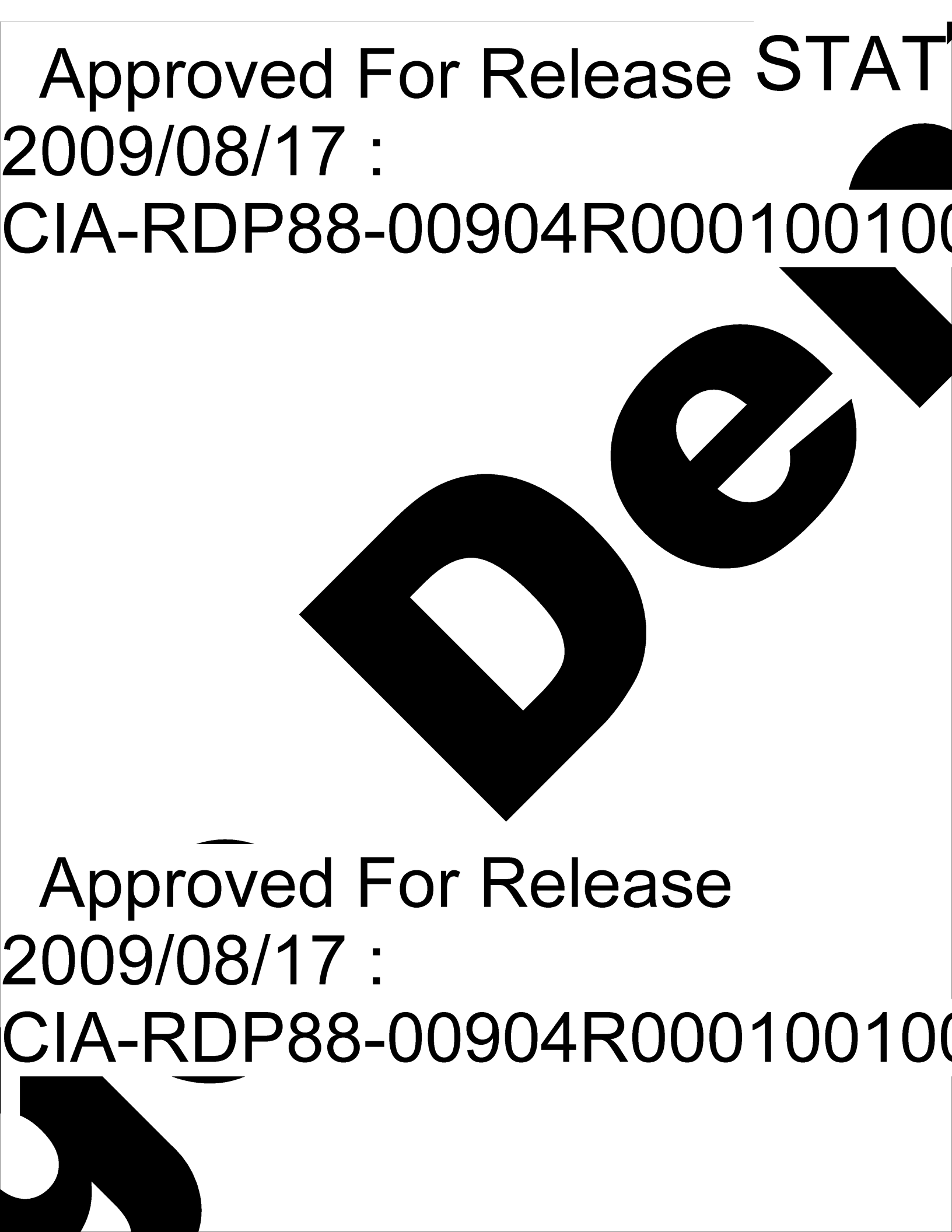

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URANIUM PREPARED BY POWDER METALLURGY TECHNIQUES

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The powder metallurgy technology of fabricating uranium billets and articles has been recently investigated in a number of countries (USA, England, France etc)[1-7,10].

Regardless of the advantages or the disadvantages, from the point of view of production, inherent in this method as compared to the conventional technology based on the reduction smelting and casting of uranium, studies of powder metallurgy technology are of independent scientific interest, as they reveal a variety of physico-chemical and physico-metallurgical regularities enriching our knowledge about uranium and its properties.

Preparation of Initial Uranium Powder

In the publications on uranium powder metallurgy the attention is first attracted by the approach to the choice of the type and the method of preparing initial uranium powder. In some investigations[1)] the powder was used obtained by hydriding cast dense uranium with the subsequent dehydriding the hydride

powder. The powder thus obtained consists of fine irregularly shaped particles with a ramified surface.

However, such a version prolongs the technology since the additional operations of hydriding and dehydriding are added to the standard technology of cast uranium production.

Besides this the active fine-grained dehydrided powder with a ramified particle surface has a troublesome property: it is readily oxidized and ignites in air.

Other papers[2-7] describe the method for obtaining uranium powder by the calcium reduction of its dioxide in the presence of a flux-calcium chloride. This method is widely used to obtain powders of a number of refractory metals (titanium, zirconium, thorium etc.).

This process being carried out above the uranium melting point results in the metal powder, consisting of spherical particles with a smooth surface. On the other hand, when carrying out the process of calcium reduction of oxides at the temperature above the calcium chloride melting point the addition of calcium chloride is known to favour the formation of coarser powder particles of the metal being reduced.

Fig.1 shows particles of two batches of uranium powder calcium reduced from its dioxide. Fig.1a shows the powder reduced without the calcium chloride addition, while fig.1b shows the one reduced with the 6w/o addition of calcium chloride to the initial charge.

Thermochemical Studies

We started our investigations with the thermochemical calculations and the experimental determination of the maximum possible temperature that may develop in the charge on account of the heat generation during the interaction of UO_2 with calcium.

The thermal analysis showed that an abrupt temperature rise indicative of the fact that the reaction started developing at an appreciable rate, was observed on heating the charge up to 800°C. Therefore we made a thermochemical calculation for 800°C as applied to the charge without calcium chloride being added. This estimation showed that at 800°C 45650 cal was generated by the reaction $UO_2+2Ca=U+2\ CaO$. If the heat is assumed not to be lost to the ambient medium, the indicated amount of heat (the heat capacity of the reaction products taken into account)may result in the charge heating up to 1330°C.

The actual maximum temperatures developed as a result of the reaction in the middle of the charge are determined experimentally as a function of the amount of the charge(table 1). The charge was loaded in the electrical furnace heated stainless steel crucibles, the inner surface of which was lined with calcium oxide.

It is seen that the experimental data support the thermochemical calculations and permit the conclusion to be drawn to the effect that at any amount of a charge the possibility of its heating up to the temperature above 1300°C is ruled out.

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Effect of the Amount of the Flux ($CaCl_2$) in the Charge on the Uranium Powder Particle Size Distribution

It is established, that the additions of $CaCl_2$ result in the coarsening of the metal powder being formed. The mechanism of this effect, discussed early for similar reactions[8,9], is basically the following:

1) melted calcium chloride dissolves some part of calcium oxide, resulted from the reaction, and thus it partially lowers the influence of the inert refractory calcium oxide that separates the particles of the metal being formed and impedes their coarsening;

2) calcium, as well as uranium dioxide are partially soluble in melted calcium chloride.

Therefore the presence of the melt activates the interaction between calcium and uranium compounds and the transfer of uranium through the melt, which also favours the coarsening of uranium particles.

Fig.2 shows the results of the experiments to study the effect of the amount of calcium chloride in the charge on the particle size distribution of the uranium powder being formed (with calcium exceeding by 50% the theoretically necessary amount). As is shown, the uranium powder particle size distribution is most flexibly affected by the alteration of the amount of calcium chloride.For example, in the charges containing 1.5-3% calcium

chloride, there are formed uranium powders from which both a fine-grained slime fraction (the particle size is less than 0.005-0.010mm) and coarse buttons more than 0.15-0.2mm in diameter are practically absent. Such powders consisting of heavy smooth spherical metal particles, are readily separated from the reaction by-products (calcium oxide, calcium chloride and calcium in excess) by treating with water and dilute nitric acid (that is known to dissolve uranium quite slowly).

The regular shape of metal particles and a variety of particle sizes are favourable for most dense packing. In loose powder the relative density is about 60%. The densification of the powder as induced by tapping, is relatively inappreciable.

Depending on the specific surface of the powder and the conditions of its treatment, at the expense of a thin oxide film, that coats the metal particles, the powder contains an oxygen impurity in the amounts of 0.2-0.3% (or about 1% UO_2).

The oxide film thickness depending on the powder oxidation degree is 0.0025-0.005mm.

The thickness of the oxide films is decreased by the above mentioned treatment of the powder with dilute nitric acid.

Hot Pressing

The high bulk density of the powder contributes to its rapid packing during hot pressing and permits this process to be carried out in open stainless steel dies; the powder should be preliminarily wetted with bensine or white spirit to remove air out of the pores between the powder particles during heating by hot pressing.

Table 1

Temperature Developed in the Charge

Charge weight, kg	Maximum temperature in the charge middle, °C
0.2	950
2	1250
5 and higher	1270-1300

Table II

Bulk Density of Uranium Powders

Amount of $CaCl_2$ in the charge, w/o	0	1.5	3	6	12	24	37
Bulk density, g/cm^3.	9.9	11.5	10.9	11.0	12.0	12.7	13.7
Tapping density, g/cm^3.	10.7	11.8	11.9	12.0	12.3	13.2	14.1

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As is shown by the chemical analyses, the carbon impurity in the hot pressed specimens does not exceed 0.04-0.06%, hence, the use of the above liquid hydrocarbons to wet the powder is quite admissible.

At a pressure of $5 t/cm^2$ and 500° the material is practically completely densified and the porous-free state is attained.

Fig.3 shows a microsection of the hot-pressed uranium billet. A porous-free structure may be seen with the initial powder particles closely attached to one another. Each of these particles consists of numerous crystallites.

Fig.4 shows an electronograph taken from an unetched section of a hot-pressed specimen on the part of the interparticle boundary.

The size and the shape of the hot-pressed specimens that have a quasi-isotropic microcrystalline structure are essentially not altered as a result of cyclic temperature changes in the α-region. After 1000 cyclic temperature changes within 20°-500° the specimen diameter was increased by 0.4%, while its height was decreased by 0.25%.

The microstructure of the specimen cyclic heat-treated is shown in fig.5.

The shape and size stability of the hot-pressed specimens is also confirmed by the tests under irradiation.

However, the physico-mechanical properties of the hot-pressed billets (see table III), resulting from the presence of an oxide film network in their structure are insufficient to counteract high thermal stresses that may sometimes develop in uranium bodies during their operation.

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Table III

Some Properties of Hot Pressed Billets

Specific weight, g/cm^3	Hardness, H_B, kg/cm^3	Tensile strength, σ_B, kg/mm^2	Relative Elongation, δ, %
18.7-18.9	250-260	up to 40	up to 0.3
Heat conductivity, λ, cal/sm.sec ^oC	up to 150^o	300^o	500^o
	0.065	0.07	0.077

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Two ways of treating hot pressed billets were investigated: heat treatment and extrusion combined with heat treatment; their aim being to break the continuity of oxide films.

Heat Treatment

A study was made of γ-annealing as well as of quenching from the γ-and ß-phases.

Fig.6 shows an unetched section, that has a structure of a hotpressed specimen, annealed at 950°. As it can be seen, the annealing resulted in the destruction of the continuous network of the oxide interlayers and in their transformation into separate point inclusions.

This phenomenon may be accounted for by the migration and the coagulation of the oxide inclusions on account of a higher oxygen solubility in γ-uranium and by its diffusion at 950°.

In addition to the discontinuity of the oxide films γ- or ß-quenching after annealing as well as quenching with the subsequent α-annealing result in the formation of a fine-grained quasi-isotropic structure (fig.7).

As it is illustrated in table V, the annealed and quenched metal shows a considerable strength and ductility increase ($\sigma_в$ is about 50kg/mm^2 and δ is up to 3.5%) as compared to the initial hot-pressed billets.

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Table IV

Extrusion Pressure, t/cm^2

Temperature, °C	Reduction Degree, %			
	80	89	97.7	95.8
500	-	8	10	13.3
550	5	7	8.3	11.8
600	-	6	7.2	10.5
640	-	5.8	6.8	10.3

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Extrusion with the Subsequent Heat Treatment

The use of hot pressed billets prepared by powder metallurgy techniques to extrude bars that are subsequently heat treated, results in high mechanical properties of the metal.

Working that destroys the continuous interparticle oxide films and transforms them into fine isolated inclusions is more effective than the described above heat treatment alone.

The previous γ-annealing which, as it was claimed above, breaks the oxide film continuity, facilitates the effect of working towards the improvement of the mechanical properties of the metal (see fig.8).

The extrusion of a bar from a hot pressed billet that was previously γ-annealed, results in the strength value of about 75kg/mm^2 with 10-12% elongation already after 70% reduction followed by heat treatment.

At the same time, the similar extrusion from a billet that was not previously γ-annealed, results in the strength increase up to 45-50kg/mm^2 only.

However, by raising the degree of reduction to 95% the similar maximum properties (σ_B=80kg/mm^2 and δ=15%) are obtained in the extrusion, no matter whether the previous γ-annealing was or was not used. This may be accounted for by the effective destruction and refinement of oxide inclusions at a high reduction degree.

The X-ray examinations of the extruded specimens show the texture with /010/ axis parallel to the extrusion direction.

ß-heating (700°) removes the initial deformation texture,

ß-quenching results in the formation of a fine-grained

quasi-isotropic structure; and the cyclic heat treatment at 20°-500° of the specimens thus quenched does not result in the alteration of their shape and sizes; the same is true of the directly hot pressed specimens.

Table IV lists the values of pressures used in the extrusion of bars from the hot pressed billets at various temperatures and reduction degrees.

Table V shows the properties of extruded and heat treated specimens.

By combining certain extrusion and heat treatment conditions high strength and ductile properties are obtained with the quasi-isotropic and fine-grained sctucture, that ensures thermal cycling and irradiation stability. The strength reaches σ_B=80-85kg/mm^2, the elongation is δ=15-20% and the torsion angle is up to 640°-670°.

Powder metallurgy techniques offer wide possibilities of further alterations of the metal properties by increasing the quantity of dispersively distributed strengthening oxide inclusions as well as by the introduction of any alloy additions to the initial powder.

Table V

Properties of Uranium Prepared by Powder Metallurgy Method as a Function of Thermomechanical Treatment Conditions

Treatment Conditions	Extension			Compression			Torsion	
	σ_B, kg/mm^2	$\sigma_{0.2}$, kg/mm^2	δ %,%	σ, kg/mm^2	δ %,%	τ_{max}, kg/mm^2	φ^o, torsion angle	
Hot-pressed billet	20-40	-	0.15	53-64	0	-	-	
Hot-pressing + γ-annealing + β-quenching	50	38	2-35	-	-	-	-	
Hot-pressing + γ-annealing + α-extrusion + β-quenching	75-85	36.5-38	15-20	-	-	86-86.5	460-545	
Hot-pressing + α-extrusion + β-quenching	75-85	-	10-15	-	-	-	-	
Hot-pressing + α-extrusion + γ-annealing + β-quenching	78-85	46-52	8.6-13	-	-	85.4-86.6	640-670	

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Fig.1a

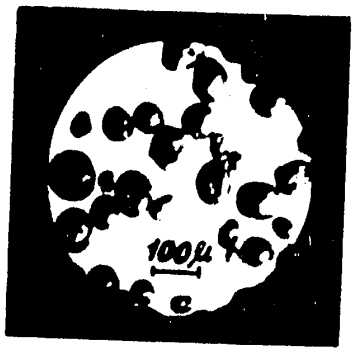

Fig.1b

Fig.1a Uranium powder reduced without addition of $CaCl_2$.

Fig.1b Uranium powder reduced with addition of $CaCl_2$(6%).

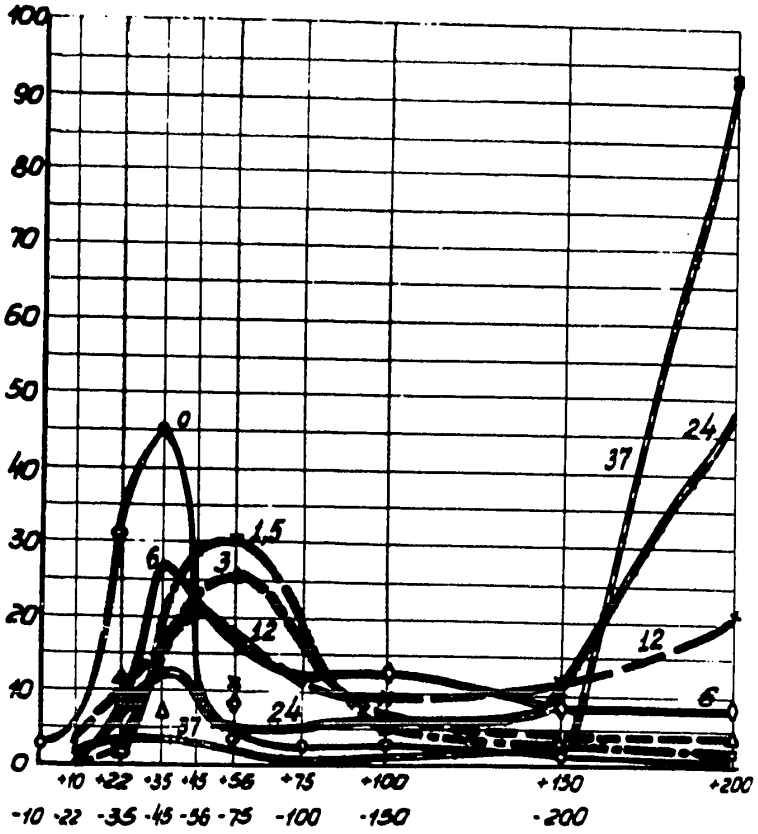

Fig.2 Uranium powder particle size distribution (weight %% of various fractions) as a function of $CaCl_2$ content in the charge (1.5%; 3%; 6%; 12%; 24%; 37%).

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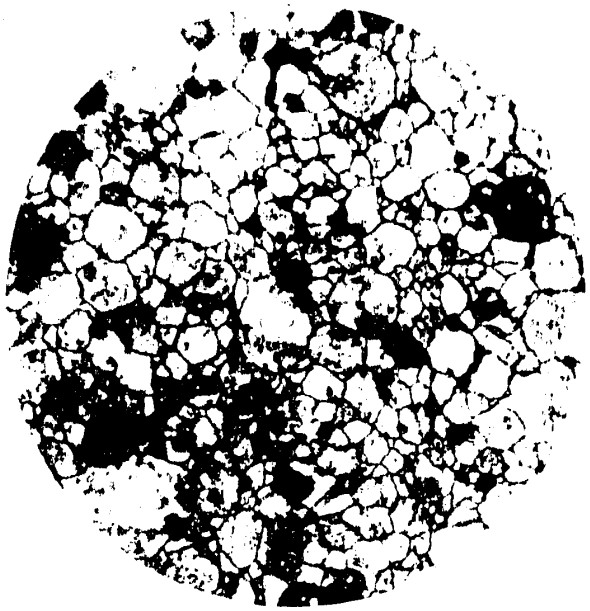

Fig.3 Etched microsection of hot-pressed specimen (x200).

Fig.4 Boundaries between particles of hot-pressed metal. Electron microscope (x8000).

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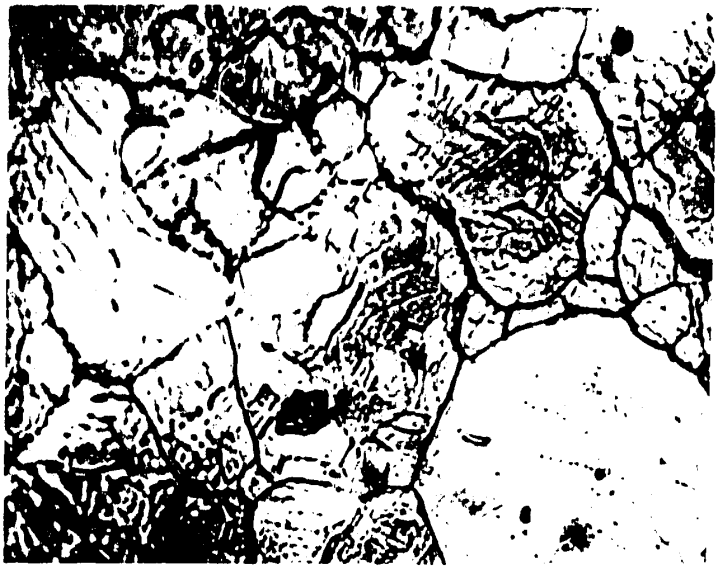

Fig.5 Microsection of hot-pressed specimen after thermal cycling. Not etched (x500).

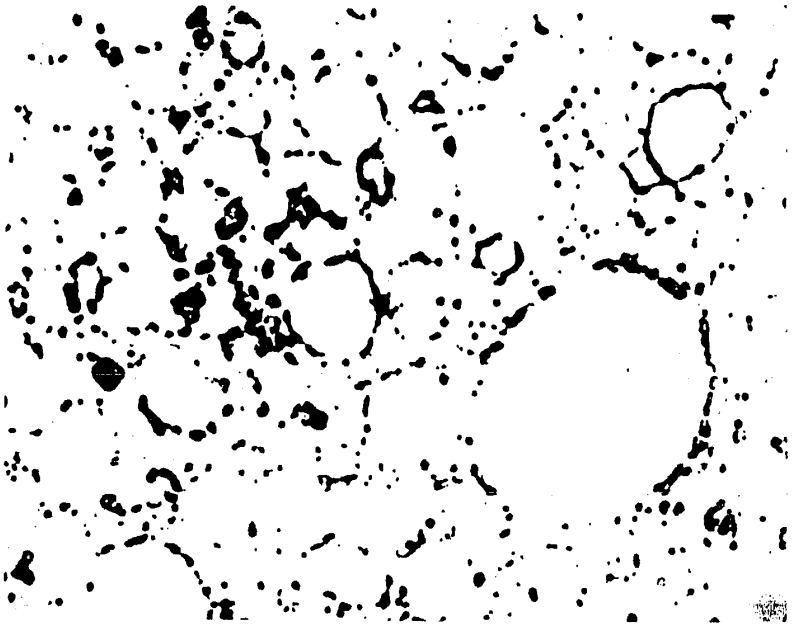

Fig.6 Hot-pressed specimen, annealed at 950°. Not etched (x200).

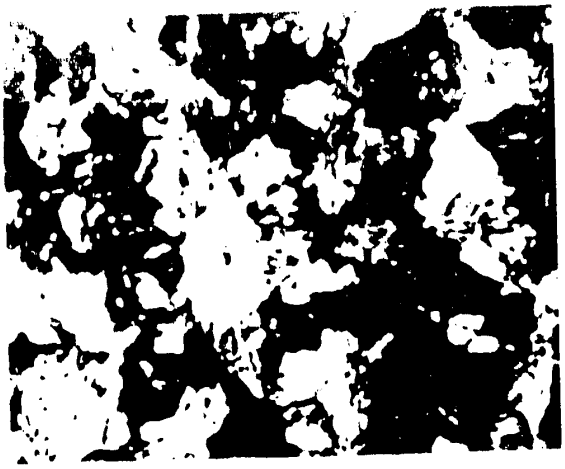

Fig.7 Etched section of hot-pressed uranium annealed at 900-950°, quenched from 750-790° and annealed at 600°(x200).

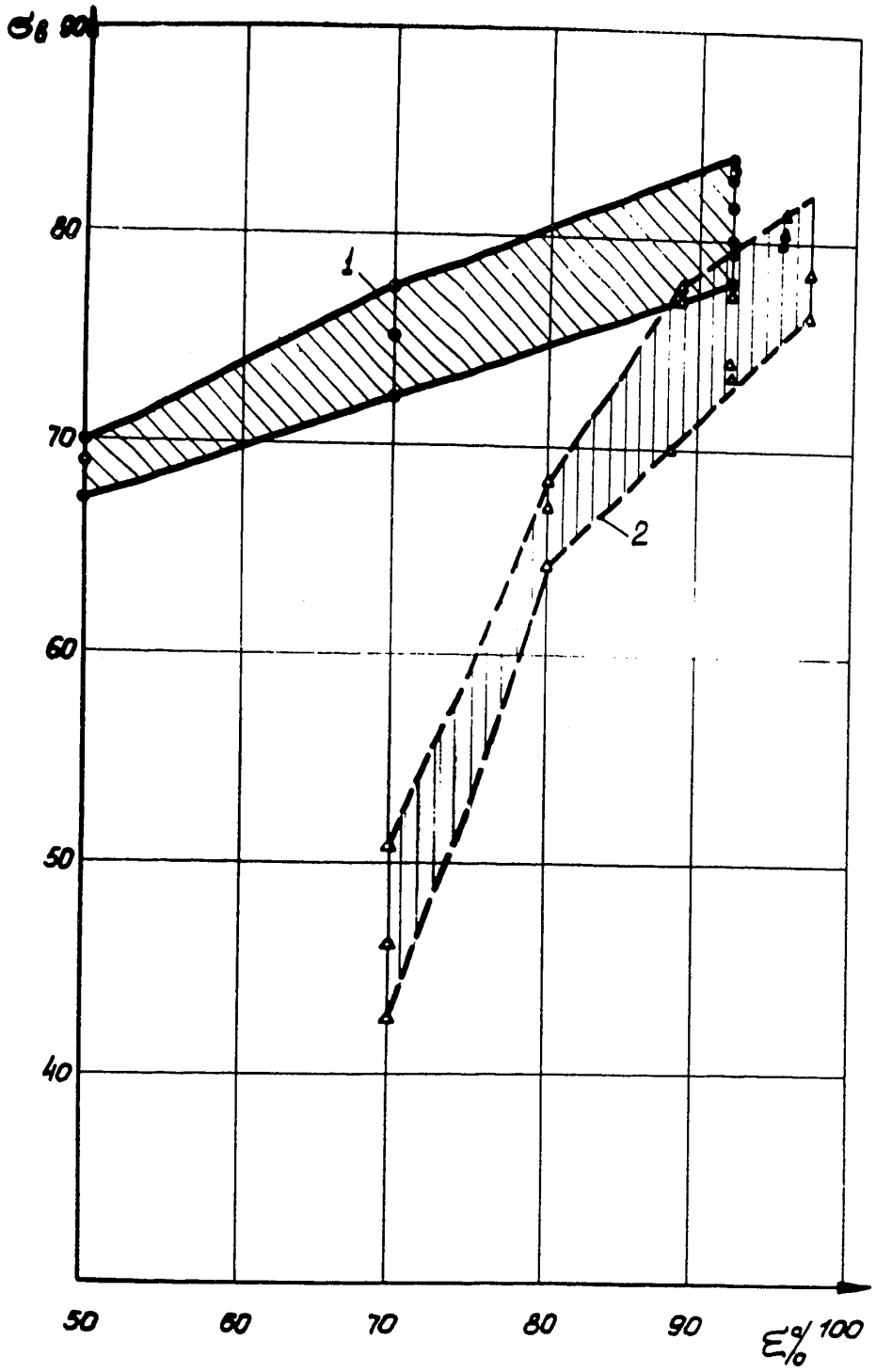

Fig.8 Ultimate tensile strength of extruded uranium prepared by powder metallurgy technique as a function of reduction (ε) and **heat treatment** conditions:

1) γ-annealing, α-extrusion, ß-quenching;

2) α-extrusion, ß-quenching.